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Oxidation behaviour of ferrous alloys used as interconnecting material in solid oxide fuel cells

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Under operating conditions in the solid oxide fuel cell (SOFC), metallic interconnect plates form electrically insulating or poor-conducting oxide scales (e.g. Cr_2O_3, Al_2O_3) at their surface which increase the contact resistance from one fuel cell membrane to the next. In order to minimize electric losses in a fuel cell stack, the formation of oxide scales on the interconnect surface must either be prevented or the oxide scale formed must have sufficient electrical conductivity. In the present work, investigations were carried out on the corrosion behaviour of different FeCrAl and FeCrMn alloys, some of which were coated with nickel (Ni). Information about ageing of these alloys on the anode side of the fuel cell was obtained by means of contact resistance measurements and scanning electron microscopy. The results reveal that FeCrMn(LaTi) alloys and Ni-coated interconnects exhibit low ageing rates and are thus suitable for use on the anode side of SOFCs.

1. Introduction

In a fuel cell, chemical energy is directly converted into electrical energy without any combustion process. The electrochemical reaction takes place between a fuel gas (e.g. hydrogen) and atmospheric oxygen. In an SOFC, oxygen ions are transported from the air cathode side through an ion-conducting electrolyte to the anode side, where the oxygen reacts with the hydrogen of the fuel gas to form water. During the recombination of hydrogen and oxygen into water, electrons are released which can be used in an outer electric circuit. Fuel cells enable an efficient and environmentally acceptable use of the available energy resources.

At Forschungszentrum Jülich, the so-called substrate concept has been developed (Fig. 1), in which an electrolyte of Y_2O_3-stabilized ZrO_2 (YSZ) and a cathode of lanthanum strontium manganite are deposited onto a 1.5 mm thick "substrate" anode of Ni/YSZ [1, 2].

The open circuit voltage of such a fuel cell membrane is about 1 volt. In order to obtain higher voltages it is advantageous to stack these cells, i.e. the anode and the cathode (which have to be supplied with hydrogen and oxygen, respectively) of two adjacent fuel cells face each other. The separation of the gas volumes is effected by means of an interconnect. The latter must exhibit good electrical conductivity in order to ensure a flow of current between the electrodes in the fuel cell with minimum electrical losses. Therefore, the formation of insulating corrosion products at the interface between interconnect and fuel cell membranes has to be avoided as far as possible.

In order to achieve better electrical contact between the interconnect material and the anode, a Ni mesh is additionally provided [3]. On the cathode side, a contact layer deposited onto the interconnect ensures better conductance.

Chromium-containing stainless steels (e.g. 1.4742, for composition see table 1) are used at present as interconnect materials [4]. At operating temperatures of 800°C, however, these metallic interconnect steels often form insulating or poor-conducting oxide scales (e.g. Al_2O_3, Cr_2O_3) increasing the contact resistance [5–7]. In the case of the 1.4742 steel currently used, the contact resistance is increased under operating conditions by the formation of a thin electrically insulating aluminium oxide scale at the steel surface.

At Forschungszentrum Jülich, therefore, ferritic steels have been developed with a more favourable oxidation behaviour with regard to contact resistance [6]. Since quite a lot of investigations have been performed on the oxidation on the air cathode side (see e.g. [6]), the present work focusses on the behaviour of these materials on the anode side of an SOFC. The purpose of this paper is to verify the applicability of the interconnect materials, some of which are additionally Ni-coated, by means of contact resistance measurements and scanning electron microscopy.

2. Experimental

The investigations were carried out with the interconnect steels specified in Table I.

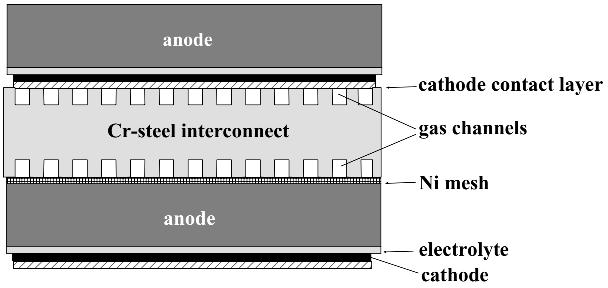

Figure 1 Contacting of a solid oxide fuel cell with a standard interconnect of a chromium-containing stainless steel with cathode contact layer.

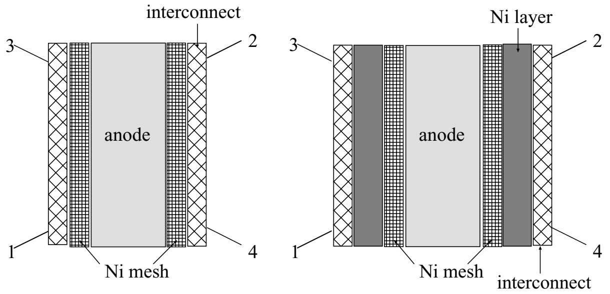

Figure 2 Measuring arrangement of the contact resistance measurements with and without Ni foil at 800°C under Ar/4 vol% H_2/3 vol% H_2O atmosphere. The lines numbered denote the voltage leads (1,2) and the current leads (3,4), respectively.

In order to remove oxide scales formed during steel manufacture, the surfaces were ground with emery paper of 15 μm roughness prior to measurement.

Some specimens were produced with Ni-plated surfaces to prevent them from forming an oxide scale on the alloy surface which would reduce the contact resistance. Coating with a 500 μm thick Ni foil was effected by uniaxial hot pressing under vacuum at 1150°C (1.4767) and 950°C (FeCrMn(LaTi)) with a hold time of one hour and a pressure of 100 MPa.

Some of the steel specimens were exposed to Ar/4 vol% H_2/3 vol% H_2O and air, respectively, at a temperature of 800°C for 100 hours prior to contact resistance measurement in order to determine the influence of preoxidation of the steel surface. In this case no Ni plating was performed.

For the contact resistance and corrosion experiments an anode substrate was sandwiched between two specimens of the interconnect steels. A Ni-mesh was placed between the anode and interconnect.

The specimens were heated to 800°C at a heating rate of 100 K/h. To measure the electrical contact resistances of the specimens, galvanostatic experiments with constant current densities of about 150 mA/cm^2 were carried out by using the four-probe dc technique (Fig. 2).

The voltage drop at the specimens was measured as a function of time at 800°C in a mixture of Ar/4 vol% H_2/3 vol% H_2O to establish an oxygen partial pressure of $p(O_2) = 10^{-15}$ bar. The maximum duration of the measurements was 3000 h.

After termination of exposure, the specimens were embedded in resin, cut perpendicular to the sandwich layers, polished and examined by means of a scanning electron microscope.

3. Results and discussion

Fig. 3 shows the curves for the contact resistance measurements of the different interconnect alloys without preoxidation.

During the heating phase and at the start of the hold time at 800°C, the NiO in the substrate was reduced to metallic Ni resulting in a considerable decrease of contact resistance in the first few hours of the measuring curve. In analyzing the values, the first five hours of the measuring time are therefore neglected.

The aluminium-containing interconnect steels, above all the 1.4767 steel with 5.7 wt% aluminium content, exhibit the highest resistance of all investigated interconnect materials. In the case of the aluminium-containing steels, a continuous, electrically insulating Al_2O_3 scale about 1 μm in thickness is formed at the interconnect surface after 320 hours of operation at 800°C (Fig. 4).

These insulating scales increase the contact resistance between Ni mesh and interconnect from about 20 to 38 mΩ cm^2 after 300 hours of operation (see Fig. 3).

Plating the 1.4767 steel with a dense Ni foil about 500 μm in thickness (99 wt% Ni) can prevent the formation of an Al_2O_3 scale at the surface of the 1.4767 steel

TABLE I Data of the interconnect alloys investigated

Steel (alloy name)	Manufacturer	Main components in wt%	Ni plating		Preoxidation of the uncoated steels	
			Yes	No	Yes	No
1.4742	Krupp VDM	80.3 Fe, 17.3 Cr, 1.04 Al, 0.93 Si, 0.31 Mn		+		+
1.4767 (Aluchrom Y Hf)	Krupp VDM	73.0 Fe, 20.4 Cr, 5.7 Al, 0.31 Si, 0.20 Ni, 0.06 Y, 0.05 Hf, 0.05 Zr	+	+		+
1.4763 (RA 446)	Rolled alloys	74.0 Fe, 25.0 Cr, 0.5 Mn, 0.39 Si		+		+
FeCrMn(LaTi) batch 1	Forschungszentrum Jülich	FeCrMn(LaTi) see [6]	+	+	+	+
FeCrMn(LaTi) batch 2	Forschungszentrum Jülich	FeCrMn(LaTi) see [6]	+	+	+	+

All contact resistance measurements carried out are marked with a "+".

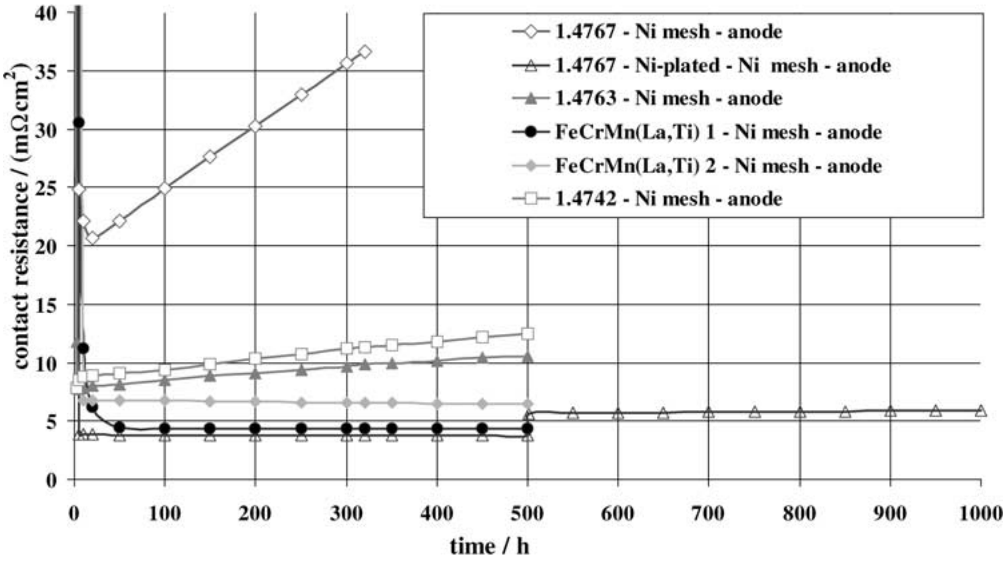

Figure 3 Contact resistance measurements with different interconnect materials at 800°C under Ar/4 vol% H_2/3 vol% H_2O atmosphere. The Ni-plated 1.4767 sample arrangement was cooled to room temperature after 500 hours and subsequently reheated to 800°C to test the thermal cycling behaviour.

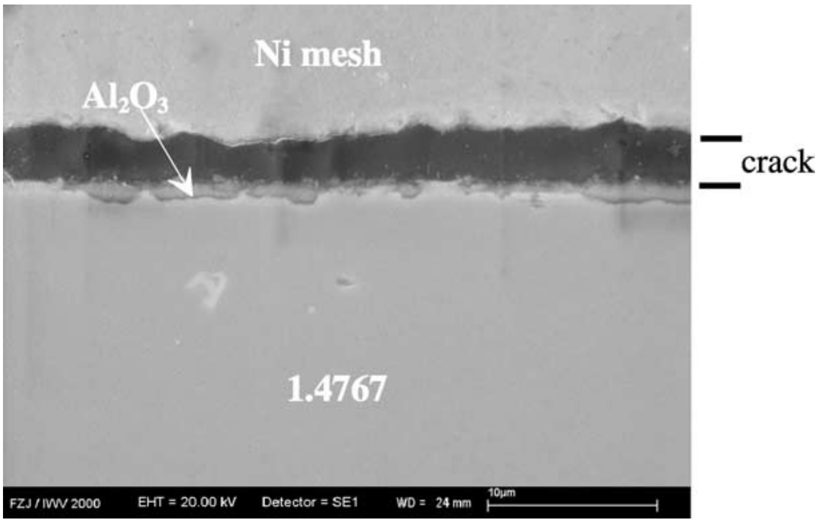

Figure 4 1.4767 steel after 320 hours at 800°C under Ar/4 vol% H_2/3 vol% H_2O atmosphere. The crack (dark area) arose during preparation.

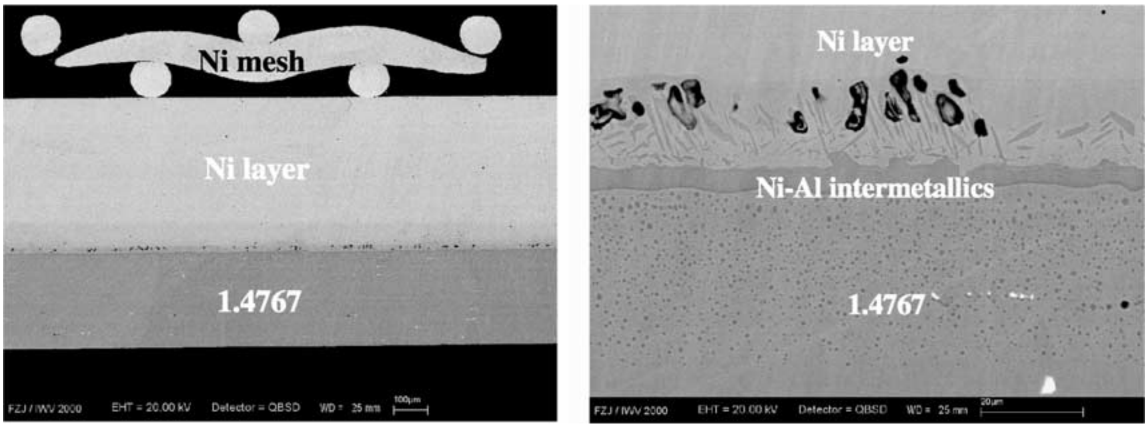

Figure 5 Micrographs of a 1.4767 foil plated with a Ni foil after 1000 hours at 800°C under Ar/4 vol% H_2/3 vol% H_2O.

so as to achieve a constant and low contact resistance for 1000 hours of operation at 800°C (Fig. 3, triangular solid symbols). A dense nickel aluminide layer was formed at theNi interface between the 1.4767 steel and the Ni foil (Fig. 5), which leads to a constant contact resistance under operating conditions. After 1000 hours, there is merely a diffusion of Cr and Al along the grain boundaries of the Ni foil, where they are insignificant

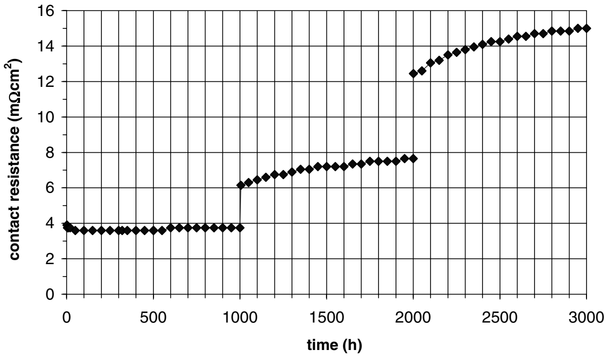

Figure 6 Long-term behaviour of the contact resistance of FeCrMn(LaTi)–Ni mesh-anode specimen at 800°C in an Ar/4 vol% H_2/3 vol% H_2O atmosphere.

for creating oxides that could lead to resistance enhancement [8]. The resistance increases stepwise when a cycling process (cooling to room temperature and renewed heating) is performed (after 500 hours).

In Fig. 5 no reference to the formation of scales is found (left). At the interface between the Ni layer and the steel, which can be seen on an enlarged scale on the right, a Ni Al intermetallic alloy is formed. This intermetallic phase ensures contact between the two layers whereas on the surface the Ni foil is in contact with the Ni mesh.

The commercial 1.4763 (RA446) alloy shows a clear increase in contact resistance (8 to 12 mΩ cm^2 in 500 hours) due to the formation of Cr_2O_3 and SiO_2 on the alloy surface.

The FeCrMn(LaTi) alloys do not show any increase of contact resistance after 500 hours of operation. The resistance values remain in the range of 4 and 7 mΩ cm^2.

In Fig. 6 the long-term behaviour of the contact resistance of FeCrMn(LaTi) is shown.

After a temperature cycling process after 1000 hours of operation the resistance increases stepwise and then continues to grow slightly. This is further intensified by further temperature cycling after 2000 hours of operation. Obviously, the cycling processes have a major influence on the contact resistance.

Repeated thermal cycling series were performed according to this procedure. Fig. 7 shows the effect of seven further cycling processes (room temperature to 800°C).

During the first few cycles there are comparatively steep jumplike increases of the resistance. Later on the thermal cycling processes no longer greatly affect the resistance; there is only a smooth increase in resistance after every temperature cycle. One reason for the greater increase of the contact resistance during the first two cycles is the rupture of contact sites by local mechanical stresses due to different thermal expansion coefficients between the Ni mesh (16×10^{-6} 1/K) [9] and steel (approx. 12×10^{-6} 1/K) [10]. The effective mechanical stresses on the other contact points are thus reduced so that this effect decreases with an increasing number of cycles.

After 1000 and 3000 hours of operation optical microscope images and electron microscope images of the interface between the FeCrMn(LaTi) were made (Fig. 8).

After 1000 hours at 800°C two layers mainly consisting of Cr_2O_3 and a spinel $(Mn,Cr)_3O_4$, respectively, of about 4 μm total thickness are found (Fig. 9). The corresponding crystal structures were detected by means of x-ray diffraction. Considerable amounts of Cr and Mn diffused into the Ni mesh and led to significant corrosion, i.e. oxidation slightly below the surface of the Ni wire (see Fig. 9). Moreover, part of the Ni from the Ni mesh is diffused into the steel.

In Fig. 10 an image of a polished and etched section of the Ni mesh is shown. The grain coarsening of the Ni in the Ni mesh and in the interconnect steel is clearly visible. This coarsening reduces the elasticity of the mesh.

With respect to these results, it can be concluded that the corrosion of the Ni mesh and its interface to the interconnect steel has a great influence on the resistance of the specimen. The lack of sufficient elasticity of the mesh might lead to a cracking of the diffusion-welded contacts between the mesh and the interconnect and the anode, respectively, mainly due to the slightly different thermal expansion of these materials. Moreover, it was found that some of the diffusion-welded junctions were broken so that there was no electrical contact. Corrosion due to the formation of oxide scales further reduces the

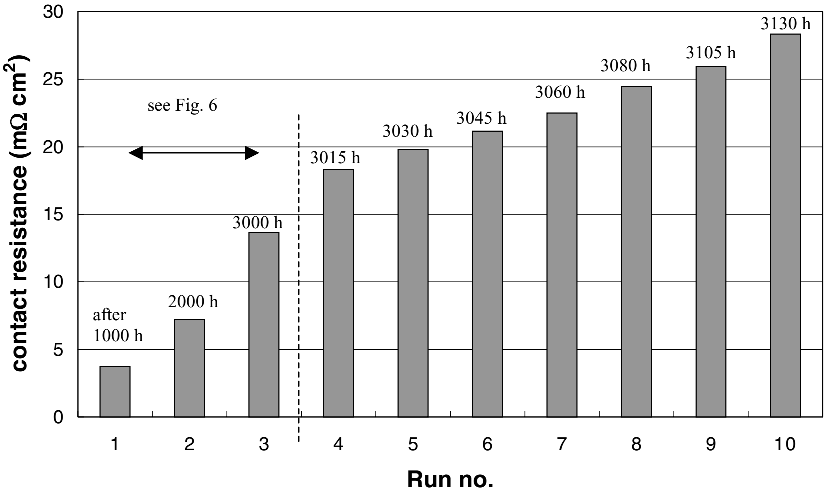

Figure 7 Thermal cycling behaviour of the sample from Fig. 6; within each cycle the sample was heated to 800°C at a rate of 100 K/h, held at 800°C for a few hours and then cooled down to room temperature. The numbers on the bars denote operating time (not including cooling time).

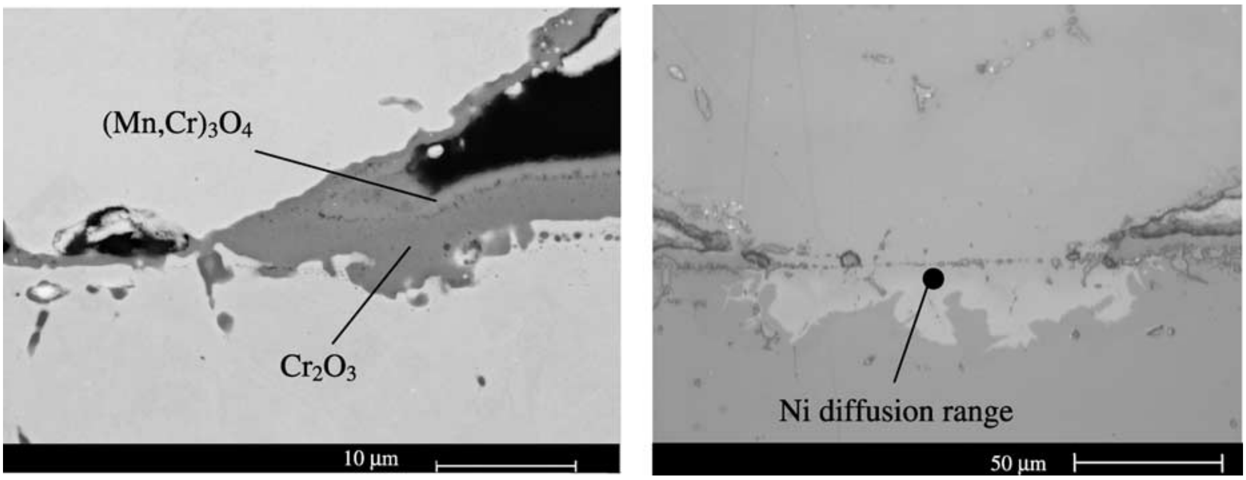

Figure 8 Micrographs of FeCrMn(LaTi) steel with a Ni mesh junction after 1000 hours (left, Cr_2O_3 and $(Mn,Cr)_3O_4$ layer visible; SEM picture) and 3000 hours (right) of operation. In order to extract the diffusion range of Ni atoms from the Ni grid into the steel ZnSe was deposited on the polished surface (optical microscope picture).

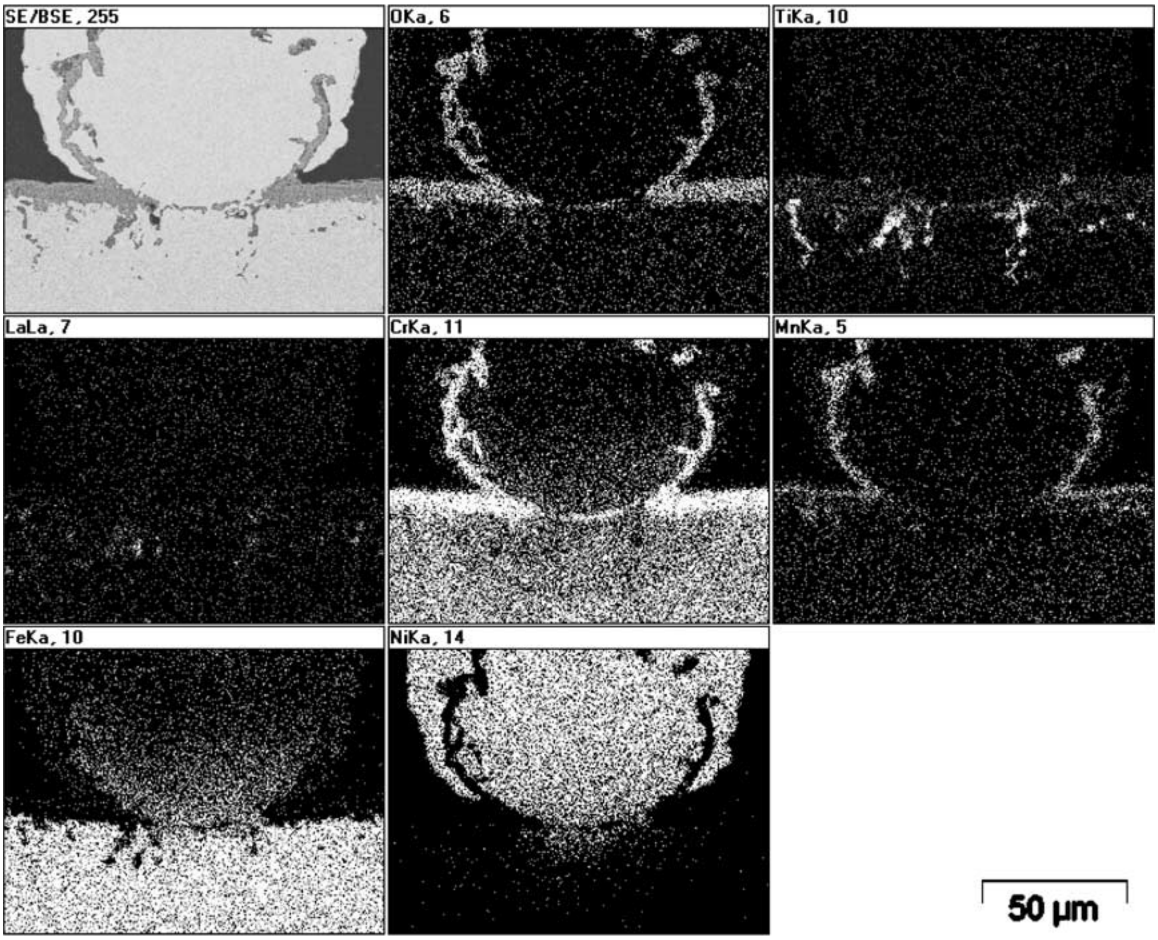

Figure 9 Micrographs of FeCrMn(LaTi) steel for periodic elements after 3000 hours of operation. The abbreviations in the image legend denote the element (e.g. Cr for chromium) and the x-ray line (Ka: K_α). The brighter a region on the image is the higher is the content of the specified element.

number of well-conducting junctions. (It should also be noted that there may be an extrinsic problem due to ageing of the sample holder which presses the anode, the Ni meshes and the steel specimens against each other. The steel of the pressure plate creeps at high temperature and thus loses its elasticity and therefore its contact pressure during operation.)

The additional plating of the FeCrMn(LaTi) with Ni only results in a slight improvement of the contact resistances. Therefore, the curves of the Ni-plated FeCrMn(LaTi) specimens are not shown in the diagram (Fig. 3) for clarity.

Fig. 11 shows the contact resistance of the FeCrMn(LaTi) alloy with and without exposure to an oxidizing atmosphere prior to measurement.

The resistance values of the FeCrMn(LaTi) alloys exposed to Ar/4 vol% H_2/3 vol% H_2O prior to measurement are several orders of magnitude higher than

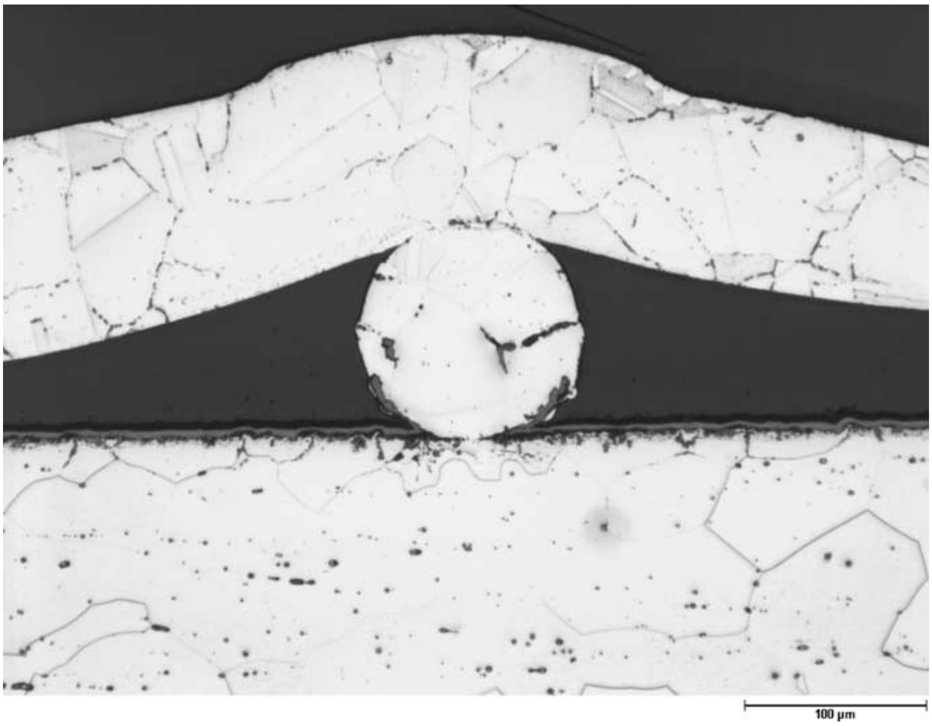

Figure 10 Polished and etched section of a FeCrMn(LaTi) steel with a Ni mesh junction after 1000 hours at 800°C.

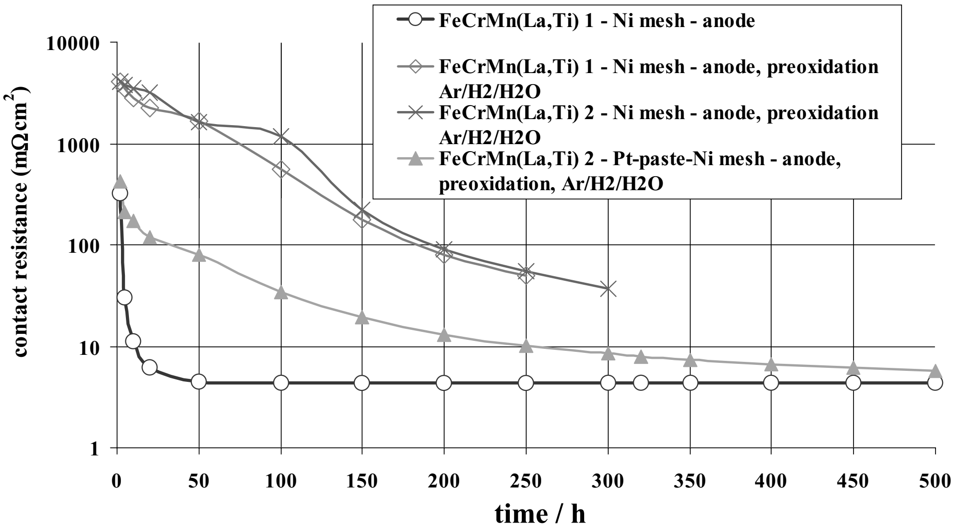

Figure 11 Measurement of the contact resistances of exposed and non-exposed FeCrMn(LaTi) steels.

the untreated specimens. This is due to the formation of insulating Cr_2O_3 and $(Mn,Cr)_3O_4$ layers which impede the flow of current.

The application of platinum (Pt) paste onto the oxidized surface of the steel leads to a signifcant reduction of the contact resistance. This can be explained as follows: Without Pt paste only a small fraction of the oxide scale near the junction between the Ni mesh and the oxide scale contributes to the electron conduction, while in the case of Pt paste on the oxide scale the current can be easily distributed along the whole surface, i.e. not only a fraction, but the complete oxide scale is used for electron conduction. Therefore—for geometric reasons—the contact resistance is lowered.

This oxide scale is also formed on the ground specimens, but the Ni mesh is diffusion-welded with the interconnect steel at operating temperature. Due to the formation of these well-conducting points, a low contact resistance is already established after a few hours of operation and remains constant for at least 500 hours (Figs 11 and 12).

In the specimens exposed to the oxidizing atmosphere prior to measurement, Ni is also diffused into the interconnect at operating temperature, but alloy formation is impeded by the oxide scale and proceeds much more slowly and incompletely (Fig. 12).

The decreasing contact resistance may be discussed in terms of defect chemistry: The resistance of Cr_2O_3 can be significantly reduced due to the incorporation of low concentrations of "reactive elements" like Y_2O_3, La_2O_3 and NiO (see e.g. [11]). In our case the La or the Ti ions diffuse into the Cr_2O_3layer, establish chemical and electronic defects leading to defect conduction. Geometric reasons may play a role, too. During operation the Ni mesh flattens slightly, thus increasing the effective contact area between Ni mesh and steel

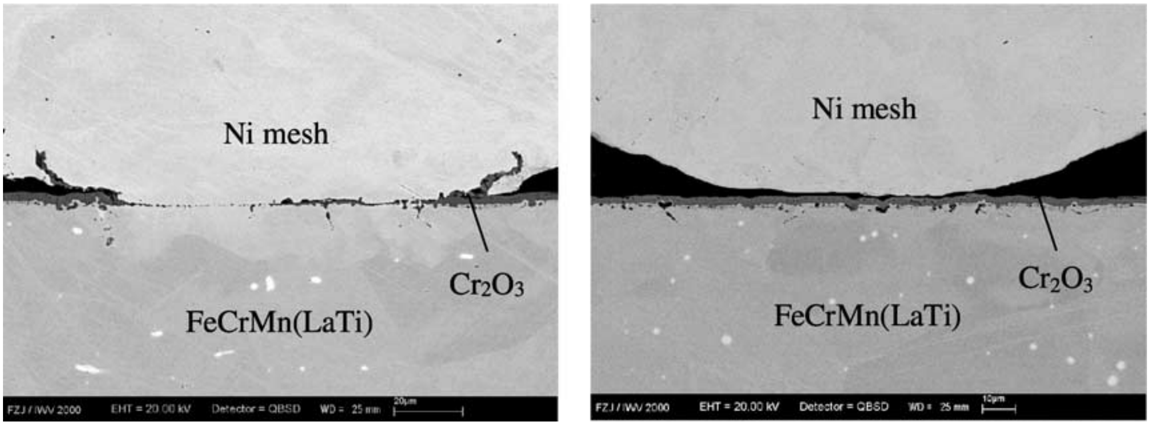

Figure 12 Micrographs of non-exposed (left) and exposed (right) FeCrMn(LaTi) steels after 500 and 300 hours, respectively, at 800°C under Ar/4 vol% H_2/3 vol% H_2O.

surface. Another reason for enhanced electrical conduction may be the spinel layer formed on top of the Cr_2O_3 layer. $(Mn,Cr)_3O_4$ spinels show a comparatively high electrical conductivity, especially in the presence of defects (e.g. alloying elements from the steel). A well-conducting layer on top of the Cr_2O_3 scale can lead to a lowering of the contact resistance, as discussed in the preceding section.

4. Conclusions

Aluminium-containing steels form Al_2O_3 scales on the surface at 800°C under Ar/4 vol% H_2/3 vol% H_2O. These insulating Al_2O_3 scales increase the contact resistance between electrodes and interconnect. A Ni plating of these steels significantly inhibits the formation of oxide scales at the surface. After 1000 hours of measurement, no indication of a deterioration of the contact resistance is perceivable. However, in using these steels, the Ni plating of the anode side of the interconnect requires a sophisticated fabrication technique, and an oxidation protection layer is also needed on the cathode side in order to prevent the formation of Al_2O_3.

The FeCrMn(LaTi) alloys investigated show similarly good resistance. However, the resistance increases considerably during thermal cycles. This is attributed to the loss of electrically well-conducting junctions due to slightly different thermal expansion coefficients of the interconnect steel and the anode material and the formation of Cr_2O_3 and $(Mn,Cr)_3O_4$ on the steel surface and in the Ni mesh. The diffusion of the Cr and Mn from the steel into the Ni mesh as well as the diffusion of Ni from the mesh into the steel, can be largely prevented by a preoxidation of the steel surface. The scanning electron microscopy studies corroborate the fact that FeCrMn(LaTi) remains stable for prolonged operating times under anodic conditions. Moreover, FeCrMn(La,Ti) is to be preferred to the aluminium-containing steel due to better processing capability and less expensive setup.

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